Electronic Supporting Information (ESI)

Convenient Tautomeric Forms in an Amino-Anthraquinone Diimine for the Generation of a Mixed-Valent "Push-Pull" Conjugated Polymer

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Experimental Section

Materials. Compound *trans*-Pt(PBu₃)₂Cl₂, and 4-[(trimethylsilyl)ethynylaniline] were prepared according to literature procedures.¹⁻³ TiCl₄, p-bromoaniline, ethynyl-trimethylsilane, triphenyl phosphine, copper(I) iodide, anthraquinone, 2-aminoanthraquinone, diisopropylamine, copper(II) bromide, PdCl₂(PPh₃)₂, 1,4-diazabicyclo[2.2.2]-octane, were purchased from Aldrich and were used as received. Platinum(II) chloride was purchased from Alfa Aeser and used as received. All reactions were performed in Schlenk-tube flasks under purified argon. All flasks were dried under a flame to eliminate moisture. All solvents were distilled from appropriate drying agents.

N,N'-bis(para-trimethylsilylethynylphenyl)anthraquinone diimine (8a).



4-[(trimethylsilyl) ethynyl]aniline (0.76 g, 4.0 mmol) and 1.35 g (12.0 mmol) of Dabco were dissolved in 25 mL of chlorobenzene while heating to 90°C. Titanium tetrachloride (0.44 mL, 4.0 mmol) were then added dropwise, followed by the addition of anthraquinone (0.42 g, 2.0 mmol) and rinsing the powder addition funnel with 20 mL of chlorobenzene. The solution was stirred at 115° C for a 12 hours period. The product was isolated by filtering off the precipitate, washed with hot chlorobenzene (2 x 20 mL). The

solution was evaporated. The solid was dissolved in CHCl₃, washed three times with water, dried with MgSO₄, and filtered. The CHCl₃ was completely evaporated leaving only the product. The product was purified on a silica column with CHCl₃ as the solvent to give disilylated compound **2a** as an orange powder. (0.99 g, 90 %). IR (KBr)/cm⁻¹v: 2154 (C=C); ¹H NMR (CDCl₃): 8.31 (2 H, t, CH aro. *J*= 7.8, 7.60 (2H, m, br.), 7.47 (5 H, d, CH aro., *J* = 8.4), 7.08 (4 H, m, br, CH aro.), 6.86 (4 H, d, CH aro., *J*= 7.5), δ 0.25 (18 H, s, Si(CH₃)₃); m/z (EI) 550 (M⁺).

2-Amino-N,N'-bis(para-trimethylsilylethynylphenyl)anthraquinone diimine (8b).



4-[(trimethylsilyl) ethynyl]aniline (0.76 g, 4.0 mmol) and 1.35 g (12.0 mmol) of Dabco were dissolved in 25 mL of chlorobenzene while heating to 90°C. Titanium tetrachloride (0.44 mL, 4.0 mmol) was then added dropwise, followed by the addition of 2-aminoanthraquinone (0.45 g, 2.0 mmol) and rinsing the powder addition funnel with 20 mL of chlorobenzene. The solution was stirred at 115^oC for a 12 hours period. The product was isolated by filtering off the precipitate, washed with hot chlorobenzene (2 x 20 mL). The solution was evaporated. The solid was dissolved in CHCl₃, washed three times with water, dried with MgSO₄, and filtered. The CHCl₃ was completely evaporated leaving only the product. The product was purified on a silica column with CHCl₃ as the solvent to give disilylated compound **2b** as an orange powder. (0.76 g, 67 %). IR (KBr)/cm⁻¹v: 2155 (C=C), 3218, 3384, 3472 (=NH, NH₂);¹H NMR (300 MHz CDCl₃): δ 8.22 (2H, m), 7.47 (6 H, d, ³*J*_{H-H} = 8.0); 7.09 (2H, m, br.), 6.86 (5H, t, ³*J*_{H-H} = 6.5), 4.06 (1H, br.), 3.70 (1H, br.), 0.26 (18H, s); m/z (EI) 565 (M⁺).

N,N'-bis(para-ethynylphenyl)anthraquinone diimine (9a).



0.55 g (1.0 mmol) of N,N'-bis(*para*-trimethylsilylethynylphenyl)anthraquinone diimine was placed in a 250 mL round-bottomed flask and 7 g of K₂CO₃ was added to the flask as well as 200 mL of a CH₃OH / THF (1:1) mixture. The reaction was stirred under Ar overnight until the solution turned orange. The excess K₂CO₃ was filtered and the remaining solvent was evaporated. The residue was dissolved in CHCl₃ and washed 3 times with water. The CHCl₃ solution was dried with K₂CO₃ and filtered. The product was purified on a silica column with CHCl₃ as eluant to give **3a**as a red powder (0.33 g, 82 %). IR (KBr)/cm⁻¹v : 2104 (C=C), 3290 (=CH); ¹H NMR (CD₂Cl₂): δ 8.62 – 8.38 (2H, m, CH aro.), 8.31(1 H, s, CH aro.), 7.63 (1H, s, CH aro.), 7.49 (5H, d, CH aro., *J* = 8.3), 7.14 (4H, s, CH aro.), 6.90 (4H, d, CH aro., *J* = 8.3), 3.14 (2H, s, CH)ppm; m/z (EI): 406 (M+).

2-amino-N,N'-bis(para-ethynylphenyl)anthraquinone diimine (9b).



0.57 g (1.0 mmol) of 2-amino-N,N'-bis(*para*-trimethylsilylethynylphenyl)anthraquinone diimine was placed in a 250 mL round-bottomed flask and 7 g of K₂CO₃ was added to the flask as well as 100 mL of a CH₃OH / THF (1:1) mixture. The reaction was stirred under Ar overnight until the solution turned orange. The excess K₂CO₃ was filtered and the remaining solvent was evaporated. The residue was dissolved in CHCl₃ and washed 3 times with water. The CHCl₃ solution was dried with Mg₂SO₄and filtered. The product was purified on a silica column with CHCl₃ as eluant to give **3b**as a red powder (0.33 g, 78 %).IR (KBr)/cm⁻¹v : 2105 (C=C), 3288 (=CH), 3222, 3385, 3474 (NH, NH₂); ¹H

NMR (300 MHz CDCl₃): δ 8.18 (2H, m, br), 7.48 (6 H, d, ${}^{3}J_{\text{H-H}} = 8.3$); 7.12 (2H, m, br.), 6.97-6.73 (5H, m), 4.08 (2H, v br.), 3.08 (2H, s)ppm; m/z (EI): 423 (M+).

Poly(bis(*para*-ethynylphenyl)anthraquinone diimine)-*trans*-bis(tributylphosphine) platinum(II) (5)



0.1 g (0.25 mmol) of N,N⁻(bis(*para*-ethynylphenyl)anthraquinone diimine, 0.17 g (0.25 mmol) of *trans*-Pt(PBu₃)₂Cl₂ and 0.01 g of CuI were dissolved in 10 mL of CH₂Cl₂. 10 mL of ⁱPr₂NH were added and the reaction was stirred under Ar overnight. The solvent was evaporated. The residue was dissolved in CH₂Cl₂ and washed 3 times with water. The solution of CH₂Cl₂ was dried with K₂CO₃ and filtered. The solvent was then evaporated and **8a** was obtained as a red powder. The polymer was reprecipitated in dichloromethane and hexane. Yield: 0.25 g, (96 %); Found: C, 62.33; H, 6.88; N, 2.69. HCl(C₅₄H₇₀N₂P₂Pt)_n requires C, 64.79; H, 7.04; N, 2.79, IR (KBr)/cm⁻¹ v : 2100 (C=C),1624 (C=N); ³¹P{¹H} NMR (CDCl₃): 3.83 (2 P, s, ¹J_{Pt-P} = 2352) ppm. ¹H NMR 400 MHz (CDCl₃) δ 8,30 (s, 2H), 7,50 (m, 3H), 7,25 (m, 5H), 7,20-6,93 (m, 3H), 6,79 (s, 4H), 2,21-2,14 (m, 12H), 1,62 (s, 12H), 1,50-1,39 (m 12H), 0,93 (t, J=7,2Hz, 18H) ppm.

Poly(2-amino-N,N'-bis(para-ethynylphenyl)anthraquinonediimine)-trans-bis(tributyl phosphine) platinum(II) (6)



0.1 g (0.25 mmol) of N,N⁻(bis(*para*-ethynylphenyl)anthraquinone diimine, 0.17 g (0.25 mmol) of *trans*-Pt(PBu₃)₂Cl₂ and 0.01 g of CuI were dissolved in 10 mL of CH₂Cl₂ 10 mL of ⁱPr₂NH were added and the reaction was stirred under Ar overnight. The solvent was evaporated. The residue was dissolved in CH₂Cl₂ and washed 3 times with water. The solution of CH₂Cl₂ was dried with K₂CO₃ and filtered. The solvent was then evaporated and **8a** was obtained as a red powder. The polymer was reprecipitated in dichloromethane and hexane. Yield: 0.24 g, (92 %); Found: C, 63.6; H, 7.14; N, 3.93. HCl(C₅₄H₇₁N₃P₂Pt)_n requires C, 63.64; H, 7.02; N, 4.12. IR (KBr)/cm⁻¹ v : 3468, 3369,3230 (NH₂), 2100 (C=C), 1624 (C=N); ³¹P{¹H} NMR (CDCl₃): 5.53 (2 P, s, ¹J_{Pt-P} = 2379), 0.47 (2 P, s, ¹J_{Pt-P} = 2304) ppm. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.32 (s, 2H), 7.68 – 7.42 (m, 4H), 7.24 (s, 5H), 6.84 (s, 4H), 4.20 (s, 2H), 2.10 (d, J = 60.6 Hz, 12H), 1.56 (d, J = 66.0 Hz, 24H), 1.03 – 0.66 (m, 18H).ppm.

Dichloro-bis(*para*-ethynylphenyl)anthraquinonediimine)di-*trans*-bis(tributyl-phosphine)platinum(II) (10a).



trans-Pt(PBu₃)₂Cl₂ (0.74 g, 1.1 mmol) and 0.010 g (5.2 x 10^{-2} mmol) of CuI were dissolved in 10 mL of CH₂Cl₂ and 10 mL of ⁱPr₂NH. 0.045 g (0.11 mmol) of N,N'bis(*para*-ethynylphenyl)anthraquinone diimine was dissolved in 10 mL CH₂Cl₂ and added dropwise over a 12 h period. The reaction was stirred under Ar overnight. The solvent was evaporated. The residue was dissolved in CH₂Cl₂ and washed 3 times with water. The solution of CH₂Cl₂ was dried with K₂CO₃ and filtered. The solvent was then evaporated and the product was purified on a silica column with CH₂Cl₂/Hexanes as the solvent to give **9a** as a red oily product. Yield: 0.11 g (60 %); Chem. Anal. Found: C, 54.92; H, 8.01; N, 2.08. C₇₈H₁₂₄Cl₂N₂P₄Pt₂ requires C, 55.94; H, 7.46; N, 1.67. IR (KBr)/cm⁻¹ v : 1624 (C=N), 2115 (C=C). ³¹P{¹H} NMR (162 MHz CDCl₃): 7.85 (s, ¹ J_{Pt-P} = 2370 Hz). ¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 3H), 7.48 (d, J = 31.8 Hz, 3H), 7.23 – 6.63 (m, 10H), 2.21 – 1.85 (m, 24H), 1.68 – 1.41 (m, 48H), 1.00 – 0.80 (m, 36H); Mass (Maldi): 1675.64 requires 1674.79.

Dichloro-2-amino-N,N'-bis(*para*-ethynylphenyl)anthraquinonediimine)di-*trans*-bis(tributylphosphine)platinum(II) (10b).



trans-Pt(PBu₃)₂Cl₂ (0.74 g, 1.1 mmol) and 0.010 g (0.052 mmol) of CuI were dissolved in 10 mL of CH₂Cl₂ and 10 mL of ⁱPr₂NH. 0.045 g (0.11 mmol) of 2,6-diamino-N,N²bis(*para*-ethynylphenyl)anthraquinone diimine was dissolved in 10 mL CH₂Cl₂ and added dropwise over a 12 h period. The reaction was stirred under Ar overnight. The solvent was evaporated. The residue was dissolved in CH₂Cl₂ and washed 3 times with water. The solution of CH₂Cl₂ was dried with K₂CO₃ and filtered. The solvent was evaporated and the product was purified on a silica column with CH₂Cl₂/Hexanes as the solvent to give **9b** as a red oily product. Yield: 0.061 g, (33 %); Chem. Anal. Found: C, 55.30; H, 7.10; N, 2.32. C₇₈H₁₂₅Cl₂N₃P₄Pt₂ requires C, 55.44; H, 7.46; N, 2.49. IR (KBr)/cm⁻¹ v : 3472, 3357, 3223 (NH₂), 2104 (C=C), 1624 (C=N); ³¹P{¹H} NMR (162 MHz CDCl₃): 8.04 (s, ¹*J*_{Pt-P} = 2383 Hz). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.41 – 8.19 (m, 2H), 7.68 – 7.41 (m, 4H), 7.23 (s, 5H), 6.84 (s, 4H), 4.19 and 4.15 (br, 2H), 2.21 – 1.82 (m, 24H), 1.65 – 1.43 (m, 48H), 1.06 – 0.73 (m, 36H); Mass (Maldi): 1688.38 requires 1689.80. N,N'-Bis(para-bromophenyl)anthraquinone diimine (11).



4-Bromoaniline (1.4 g, 8.0 mmol) and 2.7 g (24 mmol) of DABCO were dissolved in 25 mL of chlorobenzene while heating to 90 °C. TiCl₄ (0.88 mL, 8.0 mmol) was added dropwise, followed by the addition of anthraquinone (0.83 g, 4.0 mmol) and rinsing the powder addition funnel with 20 mL of chlorobenzene. The solution was stirred at 120 °C for a 12 h period. The precipitate was isolated by filtering off the precipitate, washed with hot chlorobenzene (2 x 20 mL). The solution was evaporated. The solid was dissolved in CHCl₃, washed three times with water, dried with MgSO₄ and filtered. The CHCl₃ was completely evaporated leaving only the product. The product was purified on a silica column with CHCl₃ as the solvent to give dibromide compound **11**. Yield: 1.9 g (94 %). IR (KBr)/cm⁻¹ v : 1624 (C=N). ¹H NMR (400 MHz CD₂Cl₂): 8.31 (2 H, d, *J* = 7.4 Hz, CH aro.), 7.51 (6 H, m, CH aro.); 7.14 (4 H, m, br., CH aro.), 7.61 (4H, d, *J* = 8.4 Hz, CH aro); m/z (EI): 516 (M+).

N,N'-Bis(para-bromophenyl)-9,9'-diaminoanthracene (12)



Compound **11** (0.90 g, 1.7 mmol) was dissolved in 50 mL of CH_2Cl_2 . 0.78 mL (4.3 mmol) of an aqueous solution containing HI (40%) was added dropwise into a stirred solution of **11** in CH_2Cl_2 . At room temperature the solution was allowed to stir for 30 ethynyltrimethylsilane. The reaction mixture was filtered through a fine glass sintered funnel. The solution was evaporated. The solid was dissolved in CH_2Cl_2 washed 3 times with water and dried with MgSO₄. The product was purified on a silica column with diethylether as the solvent to give diamine compound **5**.Yield: 0.55 g (61 %). IR (KBr)/cm⁻¹ v : 3386 (-NH); ¹H NMR (400 MHz CDCl₃): 8.19 (4 H, m, CH aro.), 7.46 (4

H, m, CH aro), 7.24 (4 H, d, CH aro., *J* = 8.7 Hz) 6.48 (4 H, d, CH aro., *J* = 8.7 Hz), 6.05 (2H, s, -N*H*); m/z (EI): 518 (M+).

N,N'-Bis(para-trimethylsilylethynylphenyl)-9,9'-anthracene (13).



Compound **12** (0.52 g, 1.0 mmol) was dissolved in 40 mL of toluene. 0.052 g (0.20 mmol) PPh₃, 0.070 g (0.10 mmol) of PdCl₂(PPh₃)₂ and 0.19 g (0.10 mmol) of CuI were added and stirred under Ar for 30 ethynyltrimethylsilane. 15 mL of diisopropylamine was added. Using a seringe, ethynyltrimethylsilane (0.55 mL, 4.0 mmol) was added dropwise. The solution was heated at 90 °C for 12 h. The solvent was evaporated and the product was dissolved in CH₂Cl₂, washed with water (3 x 30 mL) and dried over anhydrous MgSO₄. The solid obtained was purified using silica chromatography with CH₂Cl₂/Hexanes (30:70) as the solvent. Product **6a** was isolated as a yellow powder. Yield: 0.40 g (73 %). IR (KBr)/cm⁻¹ v: 2152 (C≡C), 3401 (N-H); ¹H NMR (400 MHz CDCl₃): δ 8.18 (4H, dd, *J* = 6.7, 3.3 Hz, CH aro), 7.46 (4H, dd, *J* = 6.8, 3.2 Hz, CH aro), 7.27 (4H, d, *J* = 8.4 Hz, CH aro), 6.51 (4H, d, *J* = 8.7 Hz, CH aro), 6.13 (2 H, s, NH), 0.22 (18 H, s, Si(CH₃)₃); m/z (EI): 552 (M+).

Instruments. All NMR spectra were acquired on a Bruker AC-300 spectrometer (¹H 300.15 MHz, ¹³C 75.48 MHz, ³¹P 121.50 MHz) or a Varian AS-400 (¹H 400.15 MHz, ³¹P 162.0 MHz) using the solvent as chemical shift standard, except in ³¹P NMR, where the chemical shifts are relative to D_3PO_4 85% in D_2O . All chemical shifts (δ) and coupling constants (J) are given in ppm and Hertz, respectively. MALDI-TOF mass spectrometry was carried out with a Waters MALDI SYNAPT HDMS using dithranol as a matrix. The mass spectra of the smaller molecules were also collected on a VG ZAB-1F spectrometer in EI mode at 70eV.The IR spectra were acquired on a Bomem FT-IR MB series spectrometer equipped with a baseline-diffused reflectance. Molecular weights and molecular weight distributions of all polymers were determined by using gel permeation

chromatography (GPC). The GPC set-up consisted of a Waters 515 HPLC pump, a Waters 996 Photodiode Array Detector and a Waters 410 Differential Refractometer, with a Styragel HR4E column (7.8*300 mm). The GPC eluent was HPLC grade THF, at a flow rate of 0.5ml.min⁻¹. Calibration curve was obtained using seven PS standards (Aldrich), with $M_{\rm n}$ ranging from 3400 to 382 000 g.mol⁻¹. UV-visible spectra were obtained on an HP-8453 diode array spectrophotometer or on a Varian Cary 300 spectrophotometer. Emission and excitation spectra were measured on a Photon Technology International (PTI) Fluorescence QuantaMaster Series OM1 spectrophotometer. The emission lifetimes were measured on a TimeMaster Model TM-3/2003 apparatus from PTI. The source was nitrogen laser with high-resolution dye laser (FWHM ~ 1400 ps) and the fluorescence lifetimes were obtained from deconvolution or distribution lifetimes analysis. The uncertainties were ~ 50-100 ps. The phosphorescence lifetimes were performed on a PTI LS-100 using a 1 μ s tungsten-flash lamp (FWHM ~ 1 μs).

Procedures for quantum yield measurements. The quantum yields measurements⁴ were performed in 2-MeTHF at 298 K. Three different measurements (*i.e.* different solutions) were prepared for each photophysical datum (quantum yields and lifetimes). The solutions for the samples and the reference were prepared under inert atmosphere in a glove box. Solutions prepared for both the reference and the samples were adjusted to obtain absorbencies around 0.06 where three different solutions for each measurement were used. Each absorbance value was measured six times for better accuracy in the measurements of the quantum yields and was adjusted to be the same as much as possible for the standard and the sample for a measurement. The reference used for quantum yield was 9, 10-diphenylanthracene^{4a} (Φ_{298K} (2MeTHF) = 1.0).

X-ray crystallography.

N,N'-Bis(para-trimethylsilylethynylphenyl)anthraquinone diimine (8a)

The crystals were grown by slow evaporation of CH_2Cl_2 at room temperature. One single crystal of 0.10 X 0.60 X 0.60 mm³ was mounted using a glass fiber on the goniometer at 294(2) K. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using ω scans. The DIFRAC⁵ program was used for centering, indexing, and data collection. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection. The data were reduced with the NRCVAX⁶ solved using SHELXS-97⁷ and refined by full-matrix least squares on F² with SHELXL-97.⁷ The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model.

N,N'-Bis(*para*-trimethylsilylethynylphenyl)-9,9'-diaminoanthracene (13).

The crystals were grown by slow vapor diffusion of MeOH on a CHCl₃ solution at room temperature. One single crystal of 0.05 X 0.50 X 0.50 mm³ was mounted using a glass fiber on the goniometer at 293 K.⁶ Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using ω scans. The DIFRAC⁵ program was used for centering, indexing, and data collection. One standard reflection was measured every 100 reflections, 10% intensity decay was observed during data collection. The data were reduced with the NRCVAX (6), solved using SHELXS-97⁷ and refined by full-matrix least squares on F² with SHELXL-97. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model.

Identification code	8a
Empirical formula	$C_{36}H_{36}N_2Si_2$
Formula weight	552.85
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a = 5.858(4) Å	$\alpha = 95.78(6)^{\circ}.$
b = 7.673(6) Å	$\beta = 96.48(5)^{\circ}.$
c = 18.842(10) Å	$\gamma = 106.26(6)^{\circ}.$
Volume	$800.1(9) \text{ Å}^3$
Z	1
Density (calculated)	1.147 Mg/m ³
Absorption coefficient	0.137 mm^{-1}
F(000)	294
Crystal size	$0.60 \ge 0.60 \ge 0.10 \text{ mm}^3$
Theta range for data collection	2.20 to 25.52°.
Index ranges	-7<=h<=6, 0<=k<=9, -22<=l<=22
Reflections collected	2730
Independent reflections	2730 [R(int) = 0.0000]
Completeness to theta = 25.50°	92.0 %
Absorption correction	Psi-Scan
Max. and min. transmission	0.9864 and 0.9223
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2730 / 0 / 185
Goodness-of-fit on F2	0.813
Final R indices [I>2sigma(I)]	R1 = 0.0936, $wR2 = 0.2024$
R indices (all data)	R1 = 0.3354, wR2 = 0.2820
Extinction coefficient	0.045(11)
Largest diff. peak and hole	0.304 and -0.206 e.Å ⁻³

Table S1: Crystal data and structure refinement for 8a.

Identification code	13		
Empirical formula	C18 H18 N Si		
Formula weight	276.42		
Temperature	293(2) K		
Wavelength	1.54176 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 5.869(2) Å	$\alpha = 95.74(5)^{\circ}$.	
	b = 7.691(3) Å	$\beta = 96.48(5)^{\circ}$.	
	c = 18.82(2) Å	$\gamma = 106.40(3)^{\circ}$.	
Volume	802.0(9) Å ³		
Z	2		
Density (calculated)	1.145 Mg/m ³		
Absorption coefficient	1.190 mm ⁻¹		
F(000)	294		
Crystal size	0.50 x 0.50 x 0.05 mm ³		
Theta range for data collection	2.39 to 70.11°.		
Index ranges	-7<=h<=6, 0<=k<=9, -22	<=l<=22	
Reflections collected	2949		
Independent reflections	2949 [$R(int) = 0.0000$]		
Completeness to theta = 70.00°	96.9 %		
Absorption correction	Psi-scan		
Max. and min. transmission	0.9429 and 0.5875		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	2949 / 0 / 189		
Goodness-of-fit on F ²	0.913		
Final R indices [I>2sigma(I)]	R1 = 0.0845, WR2 = 0.1968		
R indices (all data)	R1 = 0.1946, wR2 = 0.2447		
Largest diff. peak and hole	0.202 and -0.270 e.Å ⁻³		

Table S2. Crystal data and structure refinement for **13**.



Fig. S1. Two views of an ORTEP representation of **8a** and **13**. The ellipsoids are represented with 30% probability.

		298K	
	λ_{max} (nm)	$\epsilon (M^{-1}cm^{-1})$	
13	252	117000	254
	291	83400	308
	427	13500	452
8a	250	49600	254
	292	61000	272
	417	11000	298
			426
10a	248	67200	284sh
	293	50600	310sh
	320	44700	326
	467	14300	474
5	247	16000	300
	295	15700	322sh
	449	4230	348sh
			455
8b	250	78800	275sh
	290	92800	298
	420	20100	432
10b	243	84900	
	295	81700	304
	326sh	50900	326
	440	20300	455
6	295	14400	260
	330	12600	300
	428	6600	344
	-		460

Table S3. Absorption data in 2MeTHF

	77K		298K		$\Phi_{\rm F} 298 { m K}^{ m a}$
	λ_{max}	$\tau_{\rm F}$ (ns) and $\tau_{\rm P}(\mu s)$	λ_{max} (nm)	$\tau_{\rm F}({\rm ns})$	±10%
13	510	6.09±0.09ns (amine)	525	4.50±0.06 (amine)	0.16
80	380	$0.25\pm0.02ns$ (imina)		Not luminescent	
oa	440	2460+87 (imine)		Not fumiliescent	
10a	380	Too weak		Not luminescent	
	455	64.8±0.4 μs			
5	380	0.34±0.04ns (imine)		Not luminescent	
	460 ^b	33.4±7.7µs and			
		76.2±2.4µs (imine)			
8b	350	0.12±0.01ns (imine)			
	435°	88.1±6.8 µs and	480	0.57±0.34 (imine)	0.0010
	525	$50.0\pm5.0 \ \mu s \ (imine)$	E 4 E	4.40.0.05 (с
	535		545	4.49 ± 0.05 (amine)	_
10b	380	Too weak (imine)			
	455°	$71.1\pm0.3\mu s$	550	4(4+0,0)	0.0029
	535		550	4.64 ± 0.02 (amine)	0.0038
6	410	0.61 ± 0.04 ns (imine)		Not luminescent	
	445°	60.3±0.7 μs (imine)			
		33.2±0.4 µs (imine)			
	535	Too weak (amine)			

Table S4. Photophysical data in 2MeTHF.

a) $\lambda_{exc} = 365$ nm for all cases. b) Occasionally, the phosphorescence decays (all arising from the imine residues) were found to be bi-exponential, but for other occasions, they were single exponential with no specific trend. Moreover, the relative intensity of these components are excitation wavelength dependent, consistent with the presence of two distinct species. These components are believed to be associated with various conformations of the anthraquinone diimine units, which can form a butterfly structure (see X-ray structure in Fig. S1) or a U-shaped one. Also, *cis-trans*-isomerism is possible for the anthraquinone diimine structure depending on the relative orientation of the C₆H₄ groups to each other as well documented in reference 8. The exact identification of these conformers is not the purpose of this work. Their lifetimes are used to confirm the presence of the typical T₂ \rightarrow S₀ phosphorescence arising from the quinone diimine chromophore (see reference 5 in the text). c) Not measured. d) Heavily mixed with the phosphorescence and could not be extracted.

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